Impacts to USDWs Due to Carbon Dioxide Release from Carbon Capture and Sequestration Projects: Modeling and Experimental Studies

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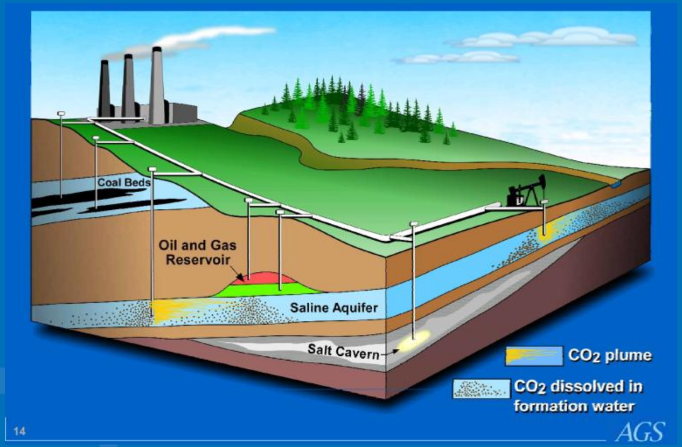


March 24, 2010
DOE/EPA Collaborative Review

ORD Research – Geologic Carbon Sequestration

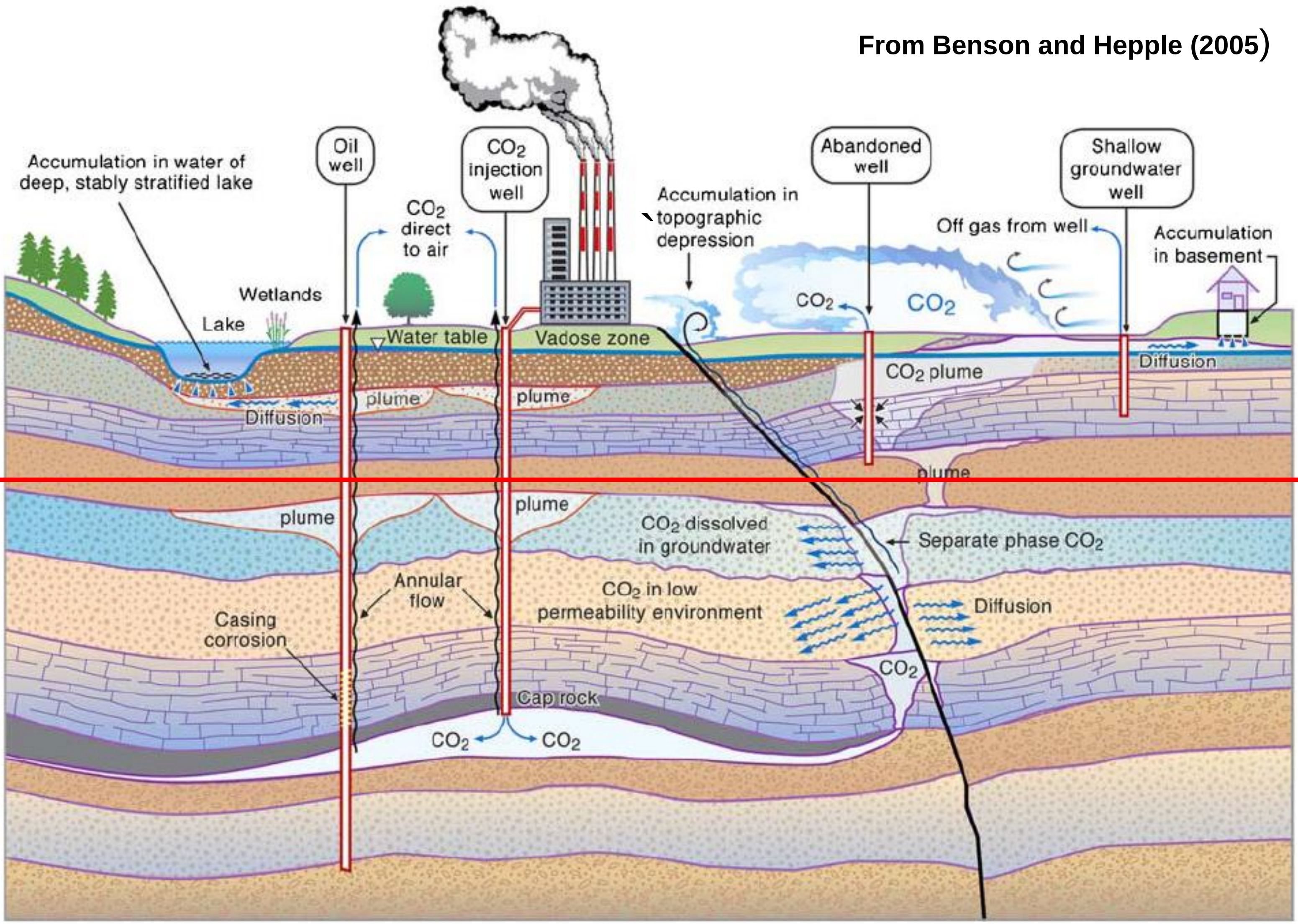
Projects Initiated Fall 2008

- Impacts to USDWs due to Carbon Dioxide Release from Geologic Sequestration Projects: Part II - Use of Soil-Gas and Ground-Water Monitoring to Detect Leakage from Plugged Abandoned Wells (Digiulio et al., NRMRL)
- Semi-analytical Models of Geologic Carbon Sequestration for Evaluation of the Area of Review, Time-Dependent Areas of Potential Corrective Action, and Leakage through Abandoned Wells (Kraemer et al., NERL)
- Impacts to USDWs due to Carbon Dioxide Release from Carbon Capture and Sequestration Projects: Part I – Geochemical Modeling and Experimental Studies (Wilkin et al., NRMRL)

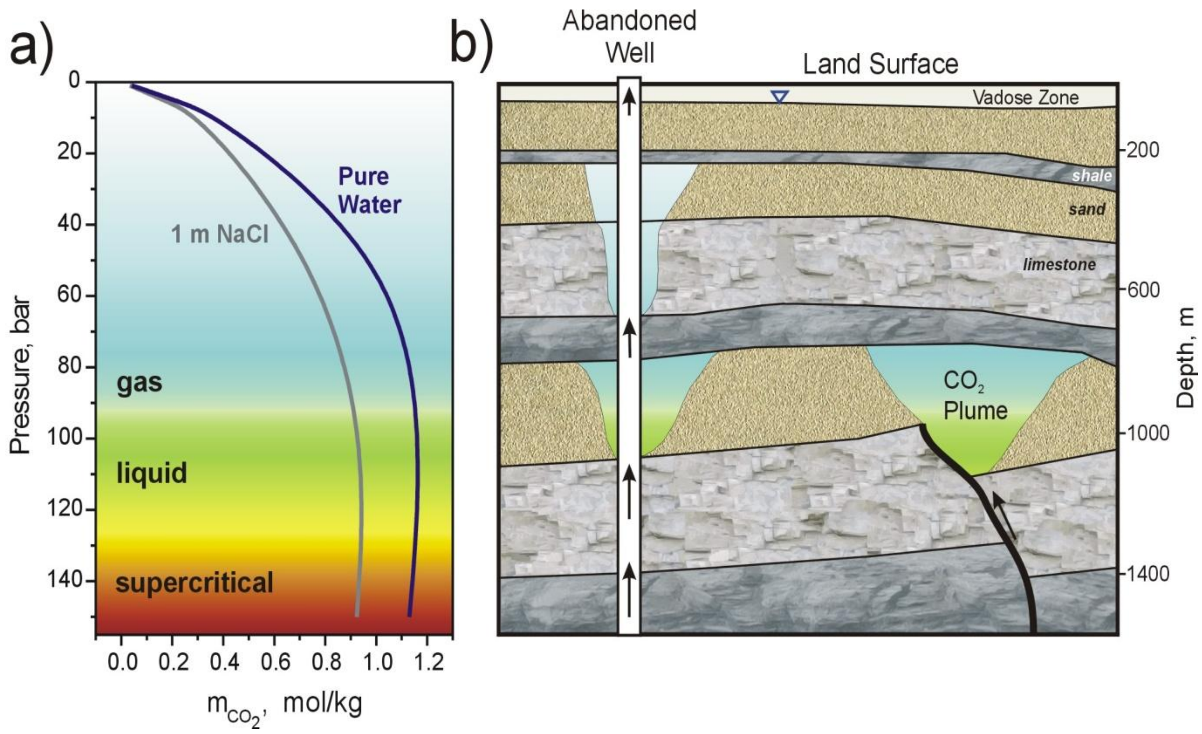
EPA United States Environmental Protection Agency

Current Research at Ada, OK Focused on Biosphere

From Benson and Hepple (2005)



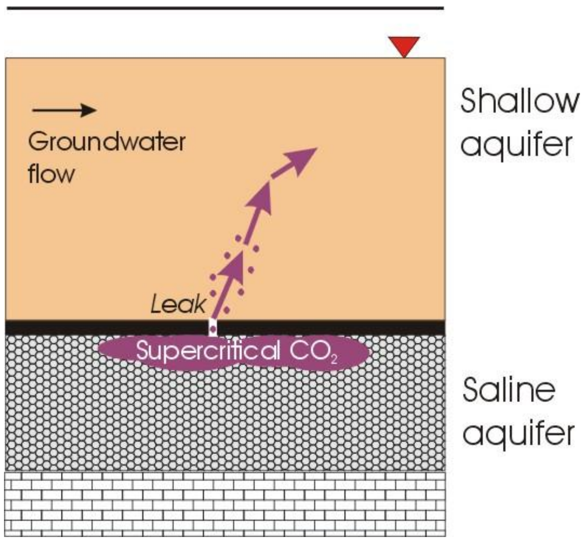
Geochemical Problem



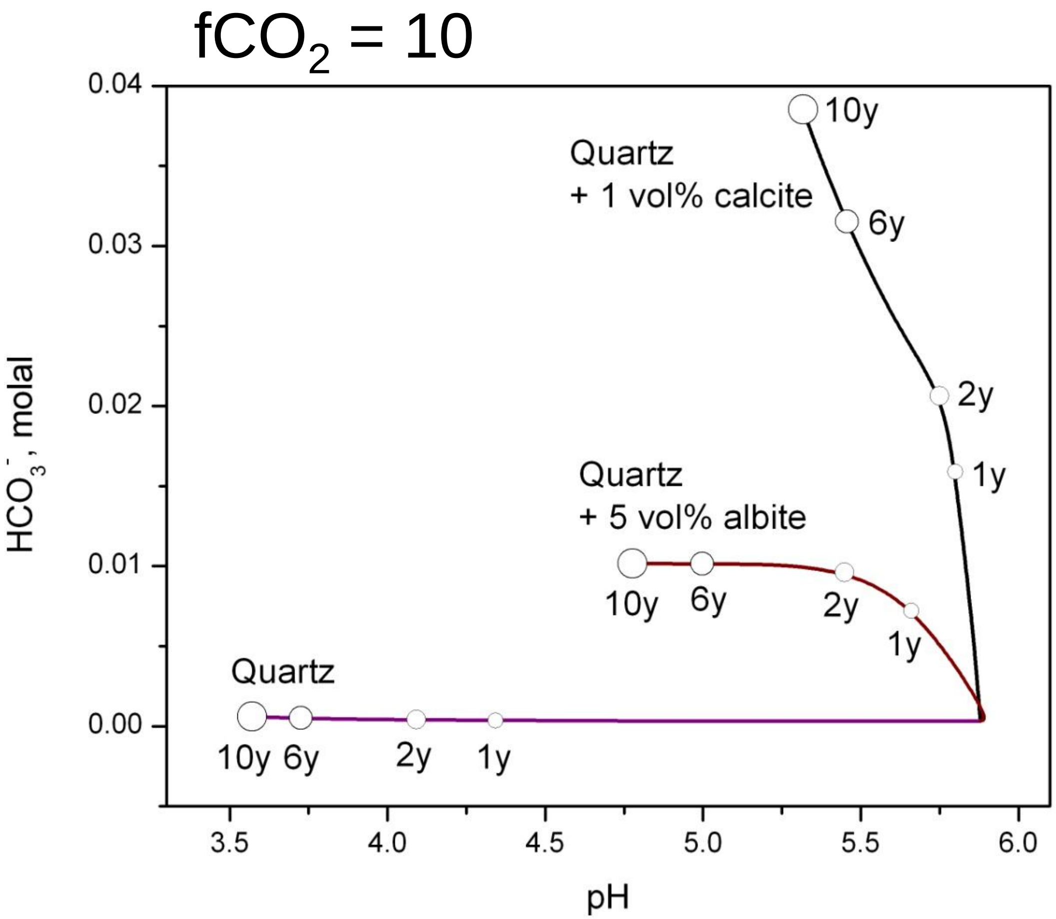
- Injection as supercritical fluid
- Leakage along T,P trajectories
- Impact of increased partial pressure of CO_2 & H_2S

1. Evaluate Impacts to USDWs due to CO_2 Release from Geologic Sequestration Projects: Modeling and Experimental Studies (Rick Wilkin and Sunkyung Choi, Ada, OK)

- pH decrease: $CO_2(g) + H_2O = H_2CO_3 = HCO_3^- + H^+$
- Trace metal solubilization
- Trace metal precipitation/sorption
- Interactions with aquifer matrix



Kinetic Modeling – Importance of Aquifer Mineralogy



- pH/bicarbonate envelopes depend on aquifer mineralogy
- Contaminant mobilization/ attenuation evaluated in context

from Wilkin and Digiulio (2010), in review

Modeling Research Tasks

- Selection of elements

  As, Ba, Be, Cd, Cr, Cu, Hg, Pb, Sb, Se, Tl, U

- Review/Comparison of Thermodynamic Data

  MinteqA2, Phreeq-C, EQ3/6, other

  Identify data gaps, uncertainties

  Update with current data

  Interagency Agreement with LBL (started 3/2010)

- Reaction Path Models/Surface Complexation Models

- Construction of Phase Diagrams

Interagency Agreement: EPA-Lawrence Berkeley National Laboratory

- Initiated March, 2010
- Richard Wilkin, Sean Porse (EPA); John Apps, Nic Spycher, and Jens Birkholzer (LBNL)
- Planned Research Output: *EPA Research Brief*

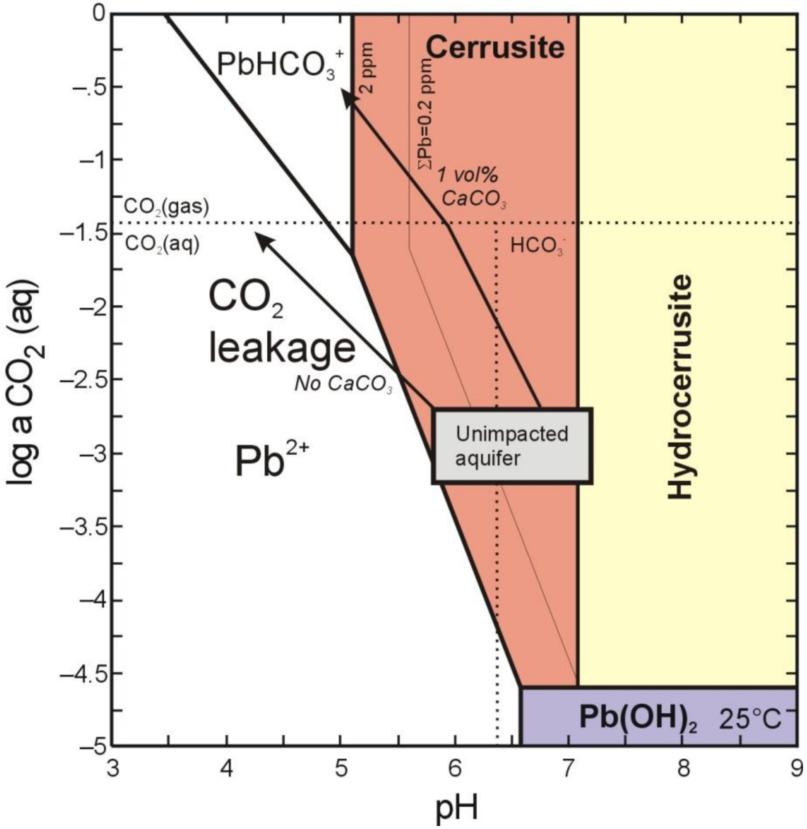
Table 1b. Solubility and ******* of Lead Carbonates and Bicarbonates and Hydroxycarbonates

Species or reaction data for standard state conditions, 298.15 K and 1 atm	Log K	Reference	
Association?			
$PbCO_3(aq) = Pb^{2+} + CO_3^{2-}$	-7.24	Hem (1976)	
	-6.60†	Bilinski and Schindler (1982)	
	-7.14	Taylor and Lopata (1984)	
$Pb(CO_3)_2^{2-} = Pb^{2+} + 2CO_3^{2-}$	-10.64	Hem (1976)	
	-10.06†	Bilinski and Schindler (1982)	
Solubility			
$PbHCO_3^+ = Pb^{2+} + CO_3^{2-} + H^+$	-13.23	Zirino and Yammamoto (1972)	
$PbCO_3(s) = Pb^{2+} + CO_3^{2-}$	-13.13	Hem (1976)	
	-13.35†	Bilinski and Schindler (1982)	
	-12.8	Wagman et al.	
	-13.21	Taylor and Lopata (1984)	
$Pb_3(CO_3)_2(OH)_2 + 2H^+ = 3Pb^{2+} + 2CO_3^{2-} + 2H_2O$	-17.64	Taylor and Lopata (1984)	
	-16.91	Mercy et al. (1998)	

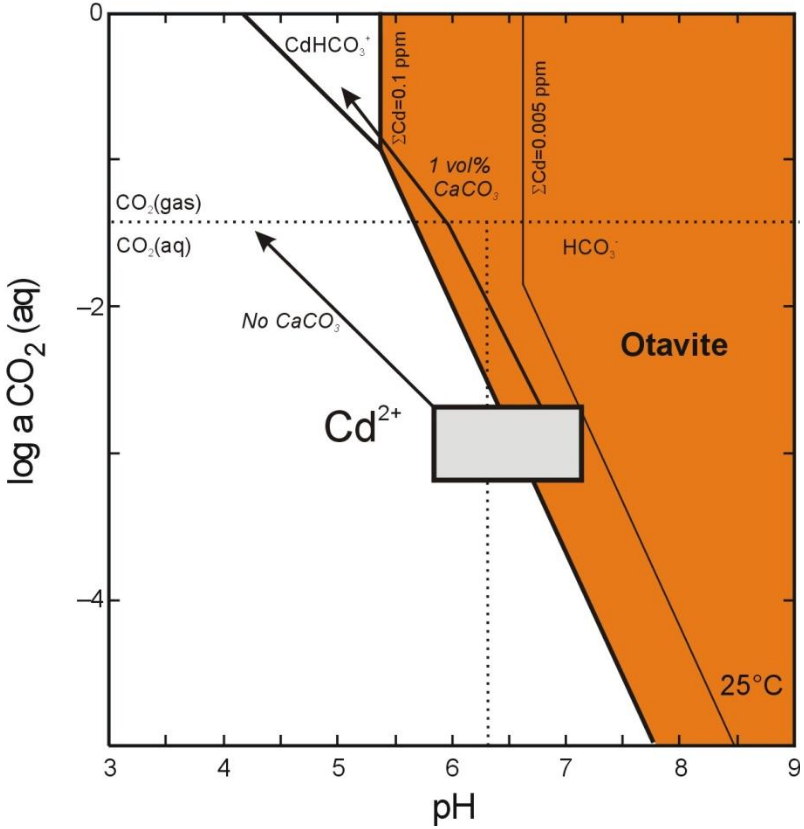
† Corrected to ionic strength = 0 using extended Debye-Huckel equation

Species or reaction data for standard state conditions, 298.15 K and 1 atm	Log K	Database	
Association?			
$PbCO_3(aq) = Pb^{2+} + CO_3^{2-}$	-6.53	MinteqA2	
	-7.24	Wateq4f	
	-6.58	V8.R6+	
$Pb(CO_3)_2^{2-} = Pb^{2+} + 2CO_3^{2-}$	-9.94	MinteqA2	
	-10.64	Wateq4f	
	-9.40	V8.R6+	
$PbHCO_3^+ = Pb^{2+} + CO_3^{2-} + H^+$	-13.23	MinteqA2	
	-13.36	Wateq4f	
	--	V8.R6+	
$PbCO_3(s) = Pb^{2+} + CO_3^{2-}$	-13.39	MinteqA2	
	-13.29	Wateq4f	
	-13.54	V8.R6+	
$Pb_3(CO_3)_2(OH)_2 + 2H^+ = 3Pb^{2+} + 2CO_3^{2-} + 2H_2O$	-18.76	MinteqA2	
	-17.46	Wateq4f	
	-18.81	V8.R6+	

Metal Solubility System: $Me\text{-}CO_2\text{-}H_2O$

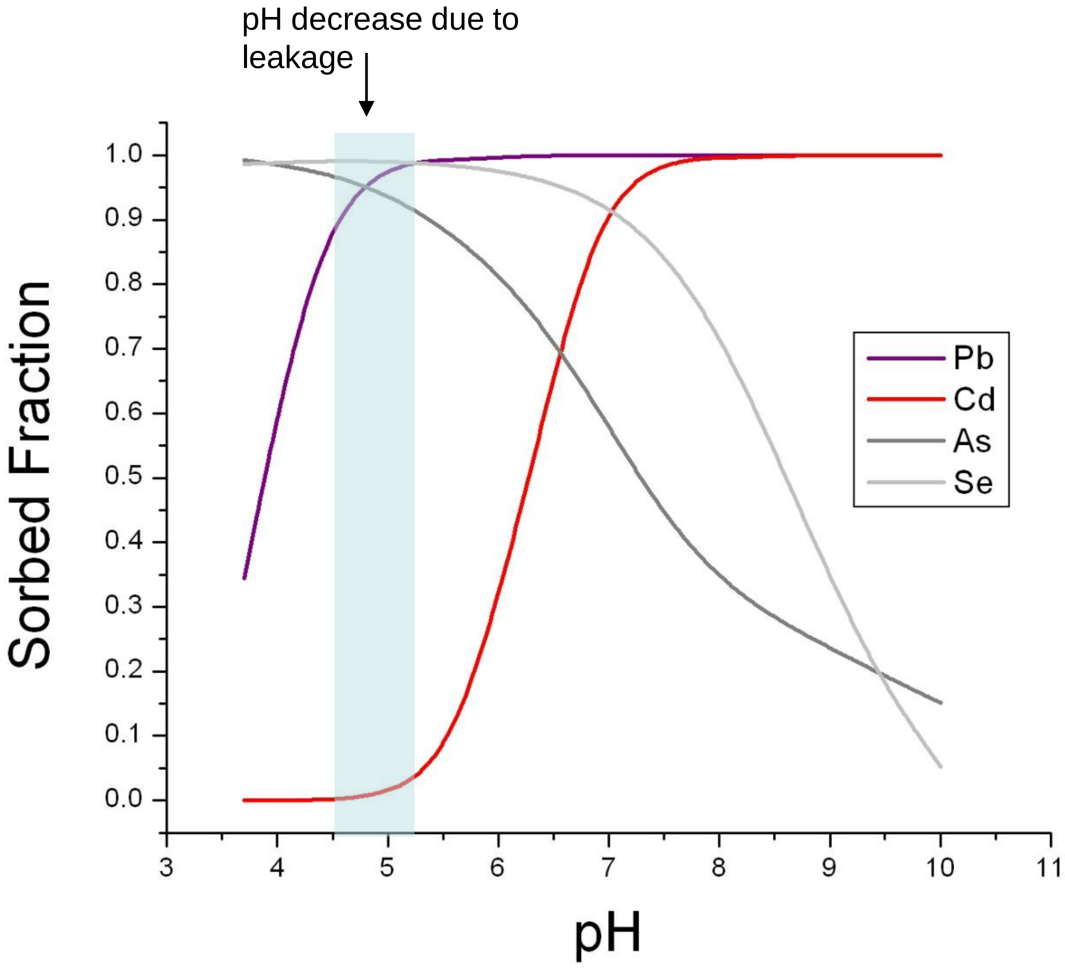


Lead



Cadmium

Surface Complexation Modeling



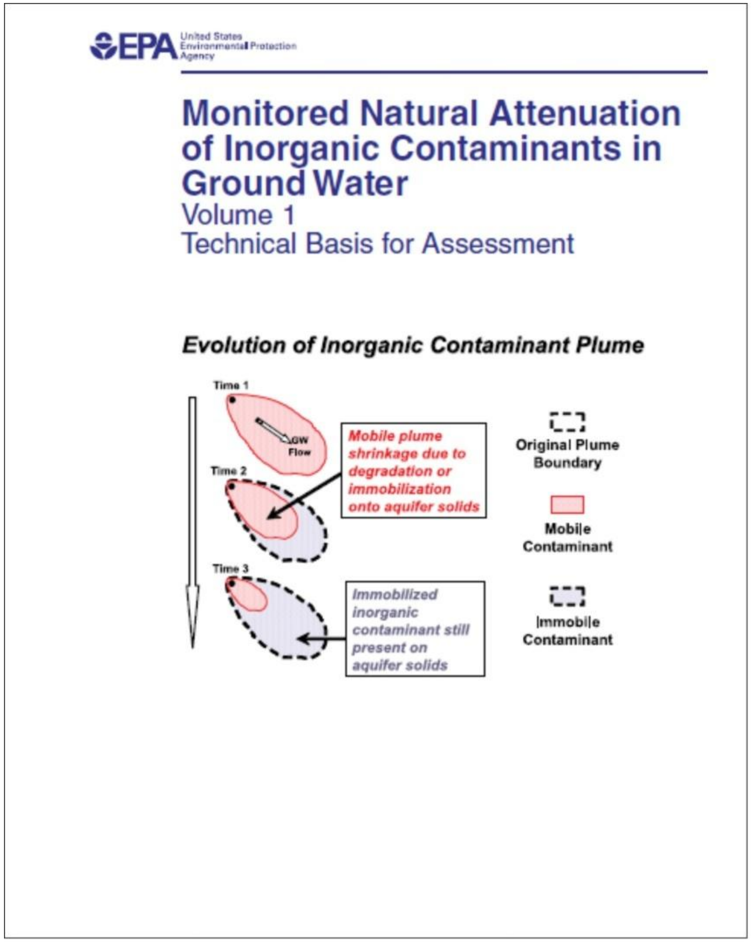
- Goethite 1 g/L
0.005 M NaCl, 2 ppm Me

- Cd expected to
be mobile at pH<5.5

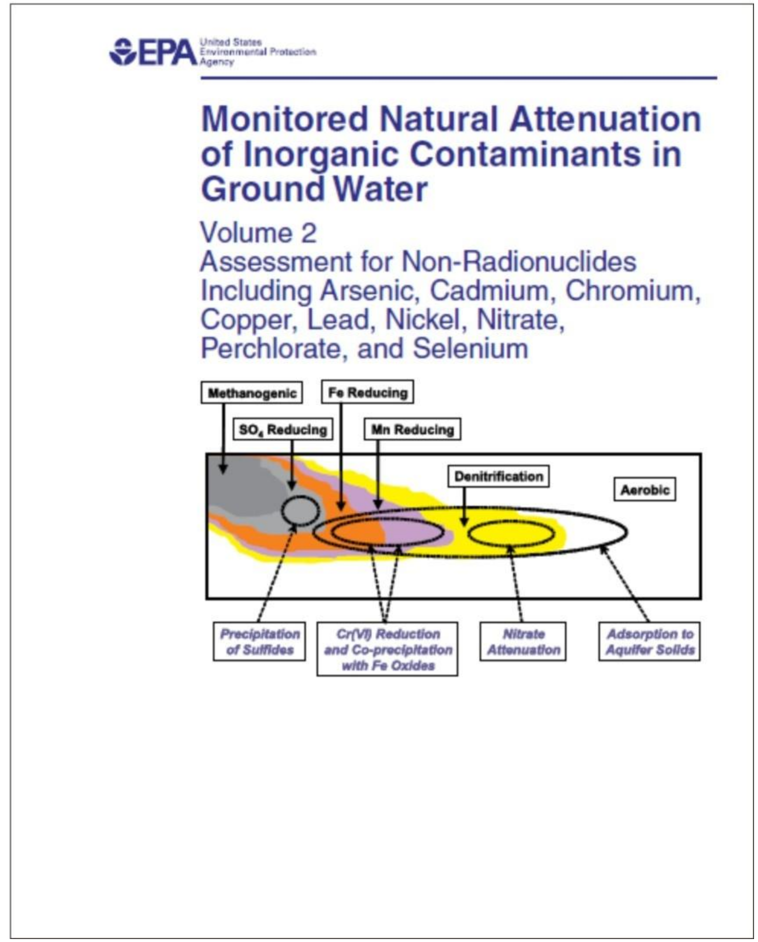
- Pb, anions immobile

- As issues

Recent EPA Reports on Monitored Natural Attenuation of Inorganics


Monitored Natural Attenuation of Inorganic Contaminants in Ground Water
Volume 1
Technical Basis for Assessment

Evolution of Inorganic Contaminant Plume


Monitored Natural Attenuation of Inorganic Contaminants in Ground Water
Volume 2
Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium

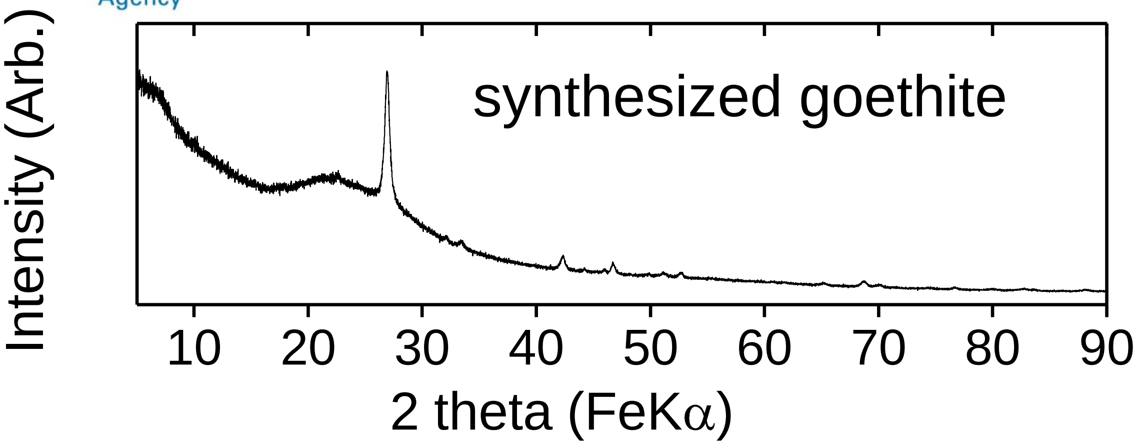
www.epa.gov/ada/publications.html

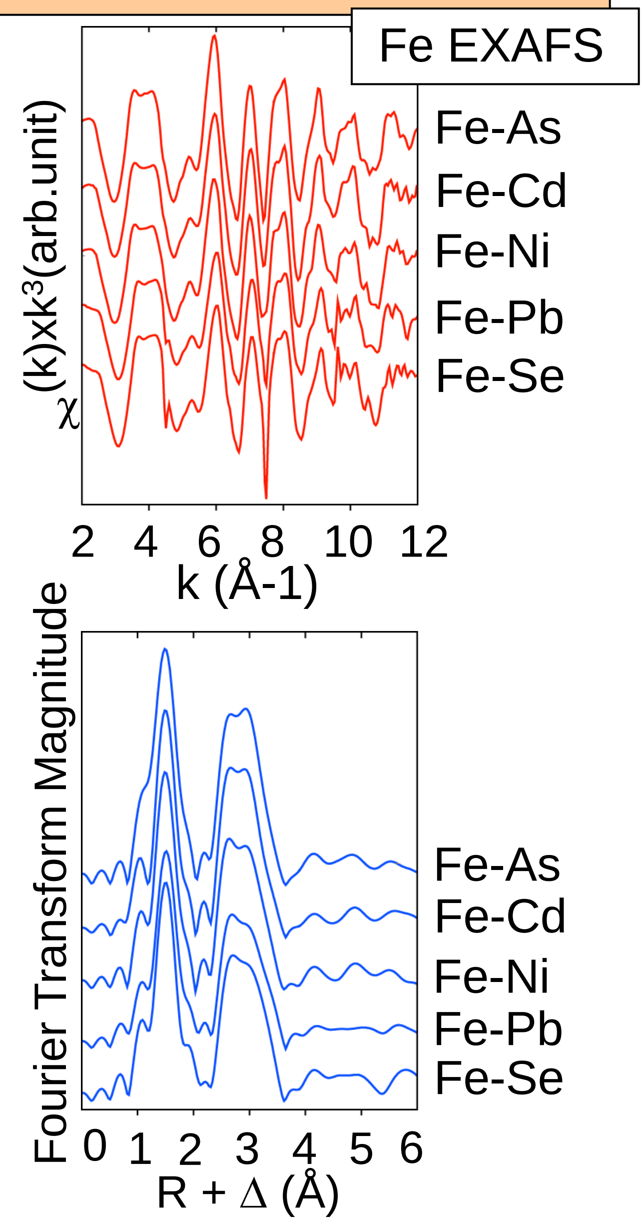
EPA United States Environmental Protection Agency

Evaluate Impacts to USDWs due to Carbon Dioxide Release from Geologic Sequestration Projects: Modeling and Experimental Studies

- Conduct column and batch-scale studies from formation (USDW) samples collected from test sites.
- Examine and simulate element partitioning and associated kinetics between selected minerals and aqueous phase over a range of CO_2 and H_2S partial pressures.
- Use results to develop sampling strategies for a controlled CO_2 injection field study.

Short-term adsorption experiments





- Material: synthesized goethite
- As, Pb, Cd, Ni and Se = [10^{-3}] M
- 1day at RT (0.005M NaCl),
- $CO_{2(g)}$ – with or without

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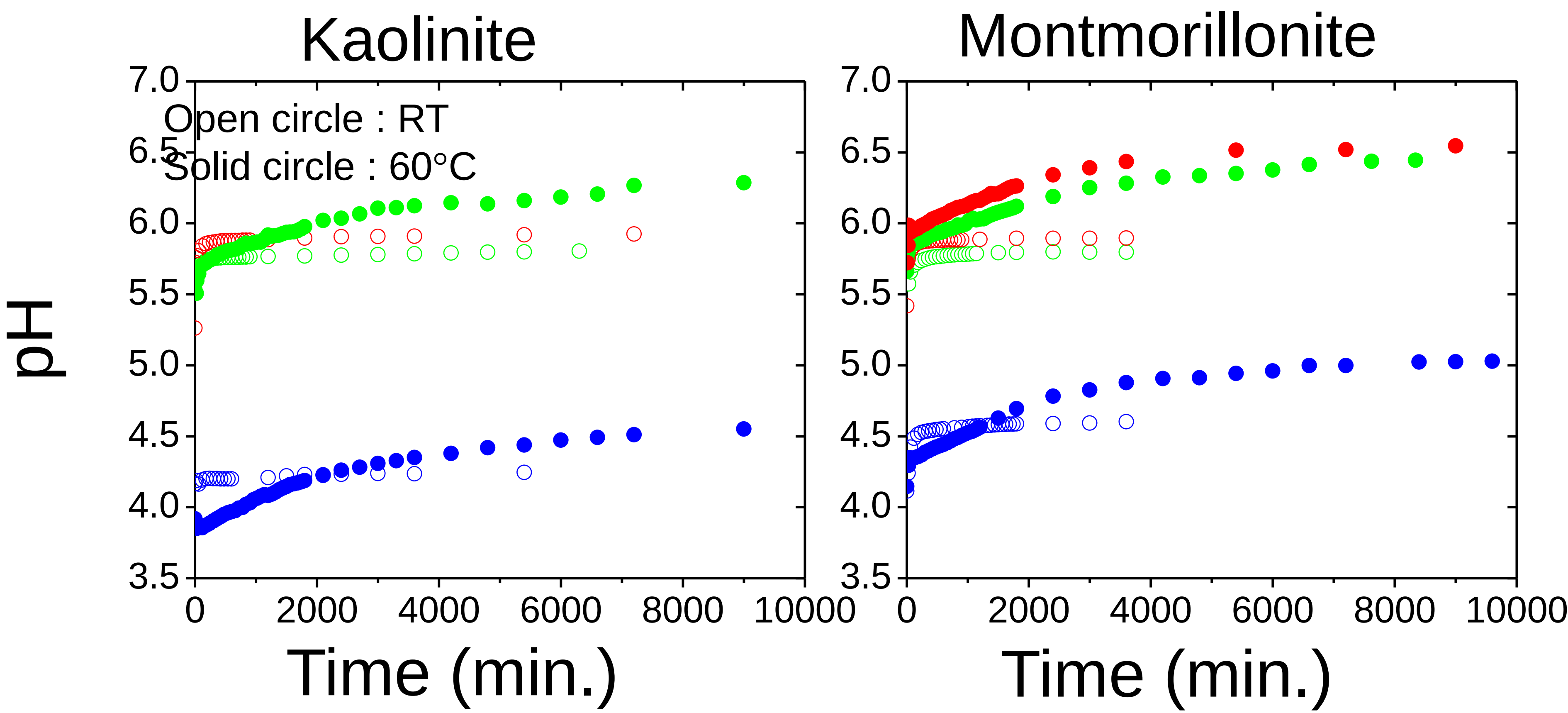
Analysis in process: Wet chemistry (ICP/MS)
Spectroscopy (Fe and As EXAFS)

pH changes after 1 day reaction



Sample + CO_2

Sample + 0.1g $CaCO_3$+CO_2

Sample + 0.2g $CaCO_3$+CO_2

Background solution: 0.05M NaCl

Ongoing experiments: short and long-term

Specimen clays (1:1 and 2:1), synthetic goethite, metal-substituted (Cd, Ni, Cr) goethite, albite, anorthite and quartz
Background solution: 0.05M NaCl, $MgCl_2$
Contaminants: As, Pb, Cd, Ni and Se (conc.: 1~3 x10^{-3}M)
Temperature (RT, 60°C), with or without $CO_{2(g)}$, and $CaCO_3$
Reacted for 1, 7, 30, 90 and 180days
solid:solution=1:50

Uptake/precipiate reaction

Reacted solutions
ICPMS/OES: As, Pb, Cd, Ni, Se, Al, Si, Fe, Ca
TIC, pH, specific conductivity

Reacted solids
XRD, SEM/EDS, HRTEM/EDS, TG/MS, FTIR, BET, Mössbauer Spectroscopy, XAS (As, Fe, Cd, Pb, Cd, Ni and Se) and micro-XAS, XRD and XRF (at APS)

Release reaction

$Mg(NO_3)_2$ extraction

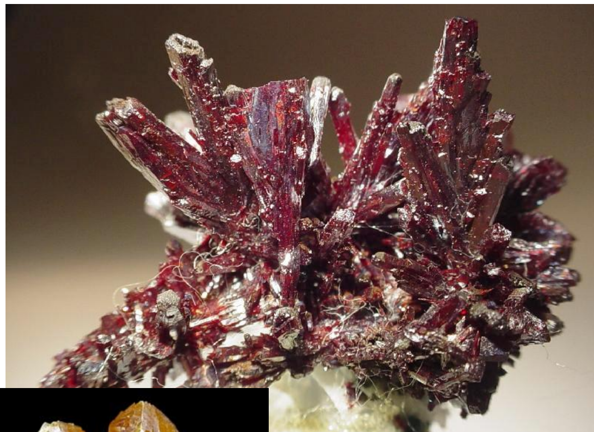
NH_4-oxalate extraction

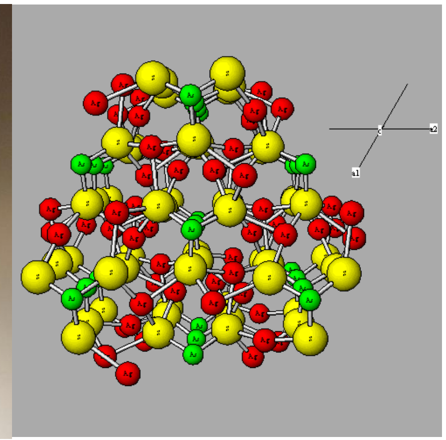
Reacted solution and solution analysis

Integrate the data and Modelling

Behavior of H_2S as a co-injectate: Interactions with Arsenic

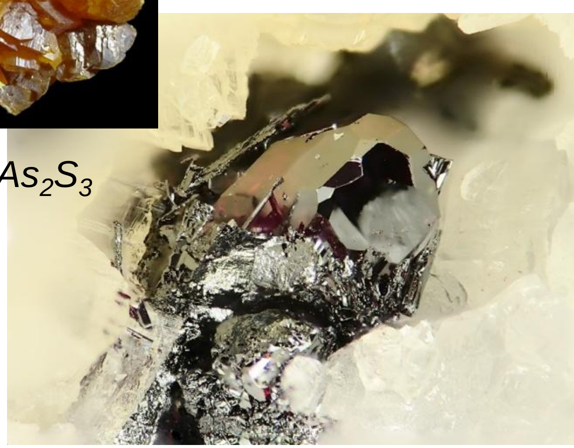
Proustite Ag_3AsS_3





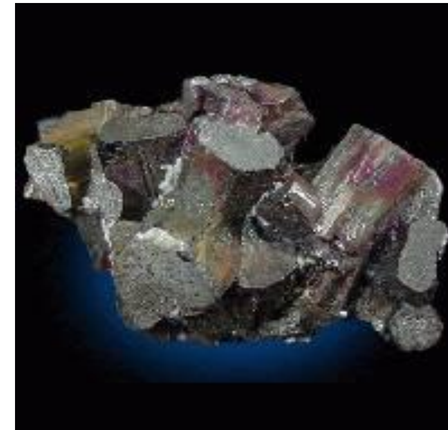
Thioarsenites As(III)-S

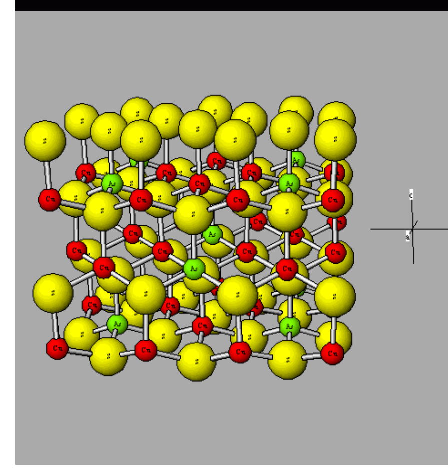
Orpiment As_2S_3



Smithite $AgAsS_2$

Enargite/Luzonite Cu_3AsS_4

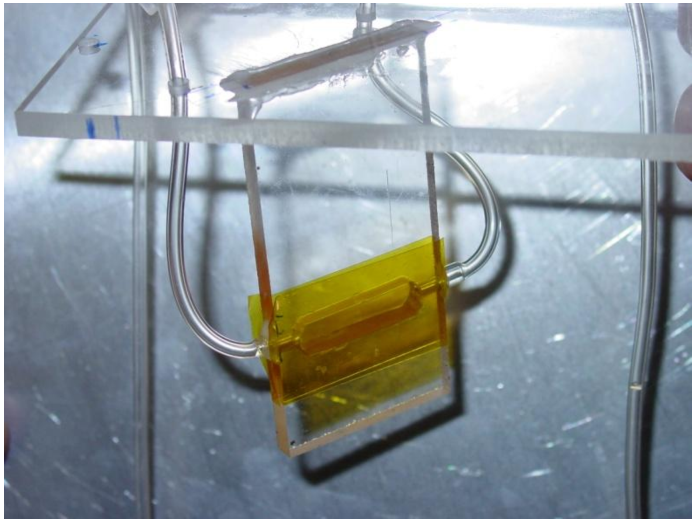




Thioarsenates As(V)-S

Mineral images
from mindat.org

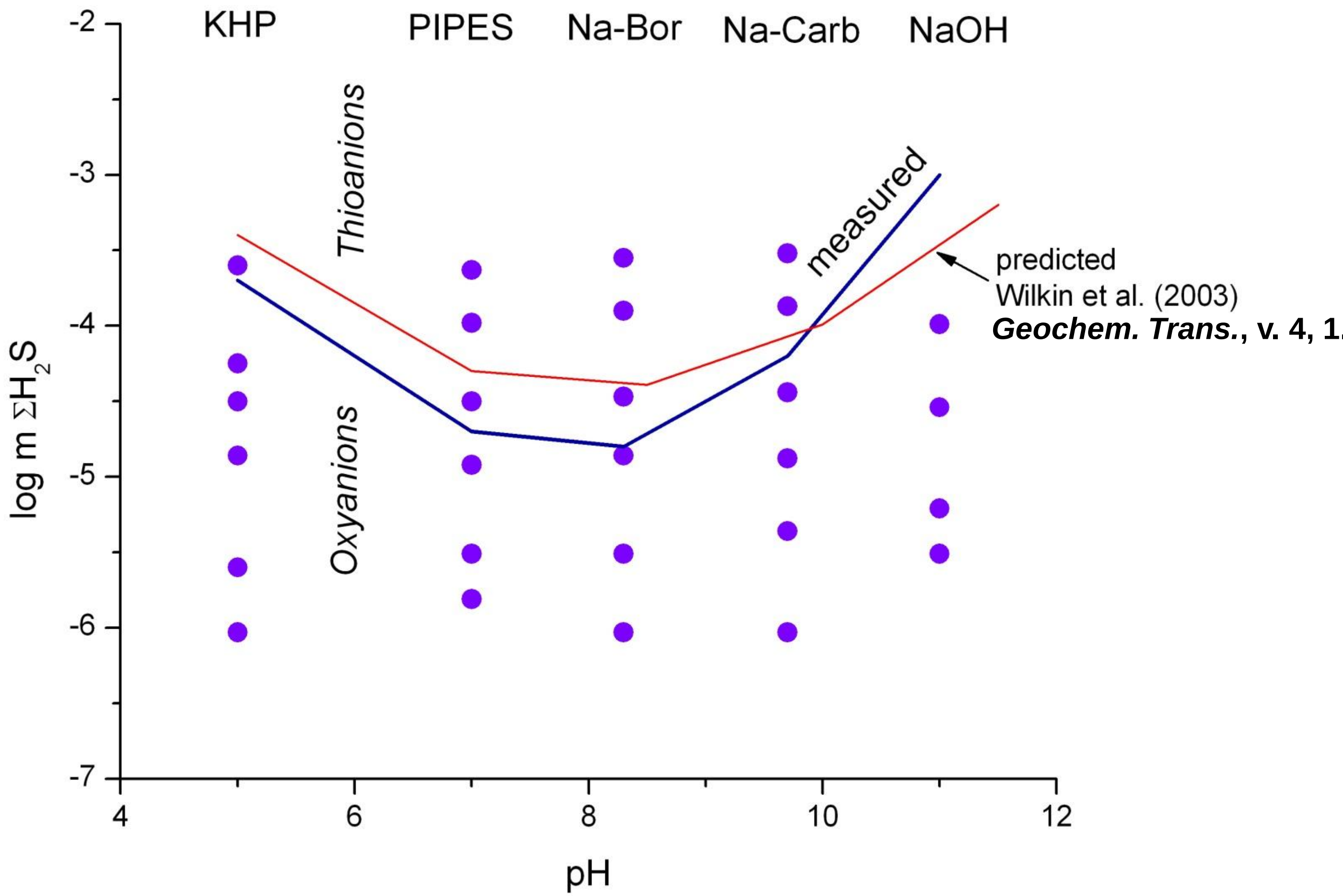
X-ray Absorption Spectroscopy for Aqueous Species: Data Collection



- XANES and EXAFS scans for oxidation state and bonding environment of As
- Arsenic mobilization potential can be increased in the presence of free sulfide

Beak and Wilkin (2008). *ES&T*, v. 42, p. 1643.

HPLC-ICP-MS: Sulfide Titration Results



Traditional Role of ORD in Regulatory Programs (e.g., CERCLA, RCRA, and UST)

- Assistance to program offices in rule making and development of guidance
- Internal and External (e.g., grants) Research
- Technical assistance to EPA regional offices and States

Internal Research ⟺ Technical Assistance